Laboratory Measurements of Temperature Dependent ^{13}C and D Kinetic Isotope Effect in the Oxidation of CH_4 by $O(^1D)$ and OH

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In this work, we utilized the frequency stabilized cavity ringdown spectroscopy (FS-CRDS) technique to study the temperature dependence of kinetic isotope effect (KIE) during the oxidation of methane by $O(^1D)$ and OH radicals. We demonstrated a dual wavelength technique by coupling two orthogonally polarized CW lasers into a ringdown cavity simultaneously to measure the full wavelength range of 1.45 to 1.65 um. The spectrometer is capable of measuring major isotopologues of methane ($^{12}CH_4$, $^{13}CH_4$, and $^{12}CH_3D$) of enriched samples to very high precision (D < 0.03% and ^{13}C < 0.01%). The photochemistry was initiated by photolyzing a mixture of N_2O, isotope enriched methane, H_2, and He at 193 nm in a temperature controlled cell between 155 K and 300 K. The concentrations of all major methane isotopologues before and after photolysis were analyzed using a frequency stabilized cavity ringdown (FS-CRDS) spectrometer. Our measurements observed D-KIE(155 K) = 1.133(20), and ^{13}C-KIE(115 K) = 1.149(22).